In situ transmission electron microscopy study on the epitaxial growth of $CoSi_2$ on Si(111) at temperatures below 150 °C

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We report an *in situ* transmission electron microscopy study on the epitaxial growth of $CoSi_2$ on Si(111) from a 10-nm-thick amorphous mixture of Co and Si in the ratio 1:2 which was formed by codeposition of Co and Si near room temperature. Nuclei of $CoSi_2$ are observed in the as-deposited film. These nuclei are epitaxial and extend through the whole film thickness. Upon annealing, these columnar epitaxial $CoSi_2$ grains grow laterally at temperatures as low as 50 °C. The kinetics of this lateral epitaxial growth was studied at temperatures between 50 and 150 °C. The activation energy of the growth process is 0.8 ± 0.1 eV.

$CoSi_2$ has a CaF_2 structure and the lattice constant is 1.2% smaller than Si. Epitaxial growth of $CoSi_2$ on Si substrates has long been demonstrated.[1,2] The formation of $CoSi_2$ by an interfacial reaction of Co metal film with Si substrate has been studied in detail.[3,4] For this Co/Si interfacial reaction, $CoSi_2$ is usually formed via a phase sequence, Co_2Si, CoSi, and then $CoSi_2$.[5] These processes are thermally activated, and usually a temperature higher than 400 °C is required to form $CoSi_2$. *In situ* transmission electron microscopy (TEM) has been used to study the nucleation and growth of cobalt silicides during the reaction of very thin Co films with Si(111) substrates.[6] Recently, single-crystal $CoSi_2$ films have been formed on Si(111) by room-temperature (RT) deposition of Co and Si in the stoichometric ratio followed by annealing.[7,8] By using this RT codeposition technique, epitaxial $CoSi_2$ can be formed at relatively low temperatures.[7] An *in situ* resistivity study showed that a codeposited amorphous film with a 1:2 Co to Si ratio crystallized on SiO_2 at 154 °C.[9] In this communication, we report on an *in situ* TEM study on the epitaxial growth of $CoSi_2$ from a codeposited amorphous film of composition Co to Si 1:2 on Si(111) at temperatures ranging from 50 to 150 °C.

The amorphous Co/Si mixture was prepared in a RIBER EVA 32 Si molecular-beam epitaxy system with a base pressure of 3×10^{-11} Torr. A 10-nm-thick amorphous film was deposited by coevaporation of Co and Si in stoichiometric ratio at near room temperature from separated Co and Si sources which were controlled by a Sentinel III deposition controller. Both plan-view and cross-sectional TEM was used in this study. The specimens for plan-view TEM were prepared by chemical thinning from the back side of Si substrates with the surface protected by wax. Cross-sectional TEM specimens were prepared by mechanical polishing followed by 5-keV Ar ion milling. The samples were always kept below 50 °C during the sample preparation procedures. *In situ* TEM analysis was carried out using a Philips PW6592 heating holder to study the growth mechanism. A thermocouple was located near the edge of the 3-mm TEM sample to monitor the temperature. The real temperature on the area being analyzed is estimated to be 30–60 °C lower than the thermocouple reading. In order to obtain an accurate temperature control for the growth rate measurement at various annealing temperatures, a furnace annealing procedure was also utilized. In this procedure, instead of annealing the sample in the hot stage of the microscope, the sample was taken out of the microscope and annealed in a furnace with a temperature accuracy of ± 2 °C. After the furnace anneal, the sample was put back into the microscope and the same area was reanalyzed. During the annealing, flow Ar was used as a protecting ambient. The growth rate was determined by comparing the size of the same epitaxial grain before and after each anneal. TEM analysis was performed in a Philips EM430 electron microscope operating at 300 kV. In the area analyzed, the substrate is one order of magnitude thicker than the $CoSi_2$ film, and consequently, can be regarded as an infinite bulk for the $CoSi_2$ flim.

Figure 1(a) shows the microstructure of an as-deposited film. The film is mostly amorphous with crystalline $CoSi_2$ embedded in it, as was observed previously.[10] All the crystalline $CoSi_2$ regions are epitaxial and rotated 180° with respect to the Si substrate (type B orientation). The number density and the size of the crystalline $CoSi_2$ regions are about 3×10^{10} cm^{-2} and 10 nm, respectively. Cross-sectional TEM shows that the crystalline $CoSi_2$ grains extend from the Si surface to the top of the as-deposited layer. This columnar structure indicates that the nucleation orginates at the Si surface and that the Co and Si atoms from the vapor phase can grow epitaxially on $CoSi_2$ nuclei near room temperature. However, the growth of epitaxial $CoSi_2$ is limited by the nucleation of crystalline $CoSi_2$. Most of the Co and Si atoms reaching the substrate surface during the RT deposition condense in the amorphous phase. In some regions the density of crystalline $CoSi_2$ is much lower, as indicated by the arrows in Fig. 1(a). These regions are bands about 30 nm wide and about 230 nm long. The bands are parallel to the ⟨110⟩ directions. The ⟨110⟩ directions are also indicated by the arrows. These bands might correspond to surface defects (e.g., steps or facets). Upon annealing, the crystalline $CoSi_2$ grows parallel to the substrate surface. Figure 1(b) shows the microstructure of the sample after being heated to a thermocoule reading of 110 °C for 17 min. The growth of $CoSi_2$ is anisotropic with a higher growth rate along the ⟨110⟩ and

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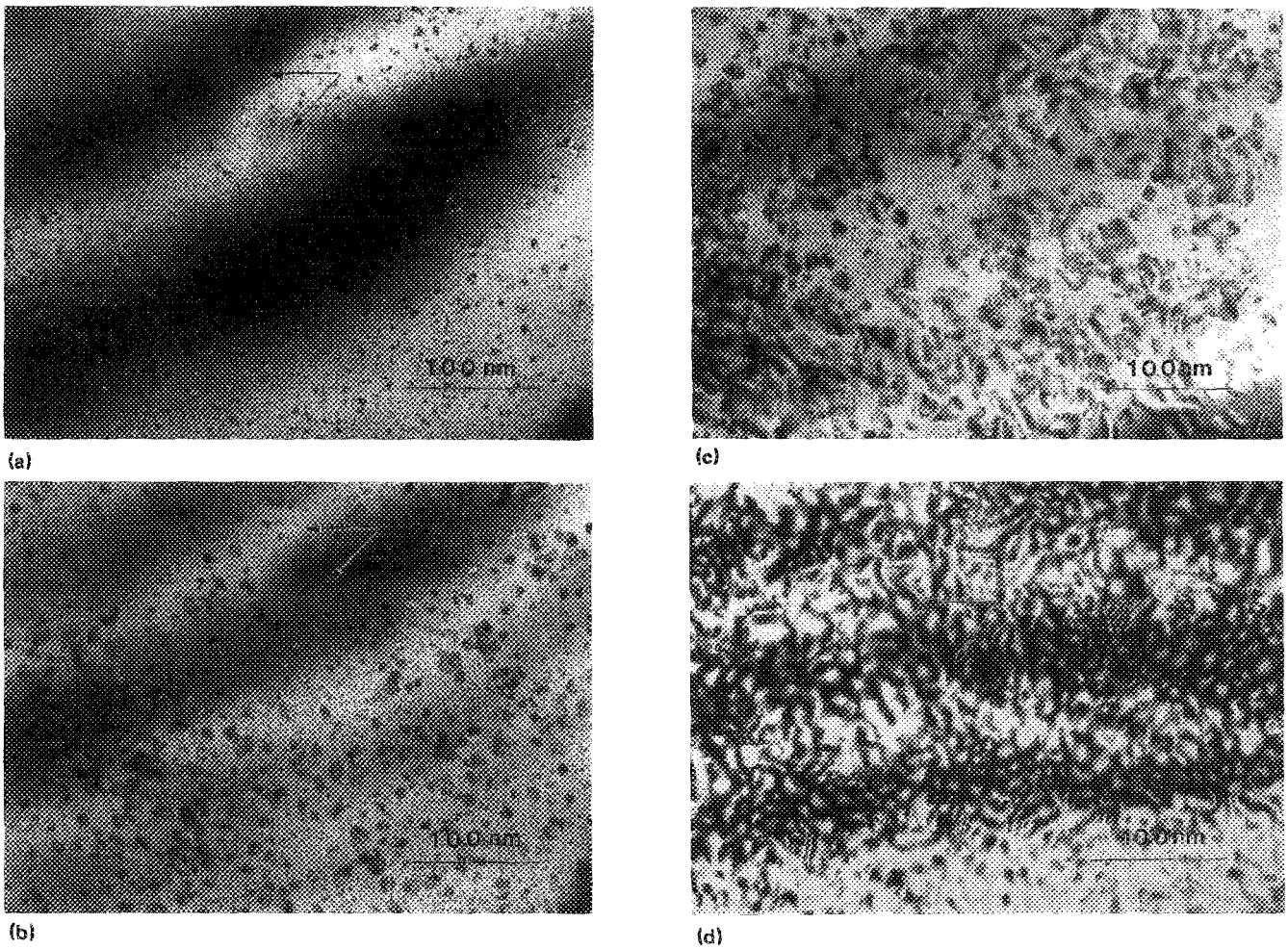

FIG. 1. Plan-view TEM micrographs showing the microstructure of a 10-nm near room-temperature-deposited Co to Si 1:2 mixture before and after the *in situ* annealing. (a) The as-deposited structure, (b) after annealing at 110 °C for 17 min, (c) further annealing at the same temperature for 22 min, and (d) after annealing at 210 °C for 60 min. The arrows indicate the bands where both the nucleation density and the growth rate for the epitaxial $CoSi_2$ are relatively low. The arrows also indicate the ⟨110⟩ directions.

⟨112⟩ directions. The $CoSi_2$ starts to coalesce after further annealing at the same temperature for 22 min, as shown in Fig. 1(c). The growth rate reduces drastically when the growing epitaxial $CoSi_2$ islands meet with the bands where the density of crystalline $CoSi_2$ is lower, as indicated by the arrows. As the temperature is increased to a thermocouple reading of 210 °C, the epitaxial $CoSi_2$ grows across the bands and forms a continuous film, as shown in Fig. 1(d). It should be noted that no additional epitaxial $CoSi_2$ nuclei are formed during the annealing. No pinholes are observed in the area analyzed which is about 100 μm^2. A parallel backscattering and channeling study showed that there is a 7% reduction of Co channeling yield from the random yield in the as-deposited sample.[11] After annealing at 80 °C, a further reduction in the Co channeling yield was observed while the width of Co channeling spectrum remains constant. This observation is in good agreement with the *in situ* TEM study.

The temperature dependence of the growth rate was studied using the furnace annealing procedure as described previously. The growth behavior and final microstructure of the $CoSi_2$ formed by furnance anneal are identical to that observed in the *in situ* TEM study. The growth rates of $CoSi_2$ along the [110] orientation at 75, 100, 125, and 150 °C are 0.1, 0.6, 2.3, and 11.5 Å/min, respectively. The logarithm of the growth rate is plotted against the inverse of the temperature, as shown in Fig. 2. The activation energy obtained from the plot is 0.8 ± 0.1 eV. This activation energy is in good agreement with the reported value (0.7 ± 0.2 eV) for the crystallization of amorphous $CoSi_2$ on SiO_2.[9] However, the crystallization rate of $CoSi_2$ on Si(111) at 150 °C measured in this study is one order of magnitude higher than that of the crystallization of $CoSi_2$ on SiO_2. The growth rate R can generally be expressed as $R = r_0 \exp(-E_a/kT)$,[12] where the preexponential term r_0 is determined by the number and effectiveness of sites available to incorporate atoms into the crystalline phase. The higher growth rate observed in this lateral epitaxial growth study indicates that the Si surface must provide new effective sites for the growth of the $CoSi_2$ nuclei.

It has been reported that the formation of Co_2Si and CoSi are diffusion controlled, with activation energies of 1.5 and 1.9 eV, respectively.[13] Also, the formation of $CoSi_2$ by the interfacial reaction of CoSi and amorphous Si was reported to be diffusion controlled with an activation energy of 2.3 ± 0.1 eV.[14] The reaction kinetics of the formation of $CoSi_2$ from a codeposited Co to Si 1:2 amorphous mixture is

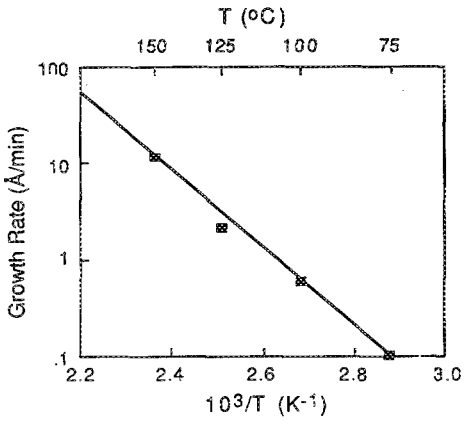

FIG. 2. Arrhenius plot of the lateral epitaxial growth rate vs the reciprocal temperature. The growth rates are determined by the furnace annealing procedure described previously. The activation energy obtained from this plot is 0.8 + 0.1 eV.

significantly simplified with no nucleation or diffusion process involved. The activation energy of 0.8 ± 0.1 eV is significantly lower than those of other diffusion-controlled reactions discussed above. To interpret this low activation energy in terms of an atomistic model is a question that is worthy of further study.

In summary, the epitaxial growth of $CoSi_2$ from a codeposited Co/Si 1:2 amorphous mixture was studied using *in situ* TEM at temperatures ranging from 50 to 150 °C. Columnar $CoSi_2$ nuclei originating from the Si surface and extending to the film surface are observed in the as-deposited film. During the subsequent annealing, the $CoSi_2$ nuclei grow laterally to form a continuous film. No additional $CoSi_2$ nuclei are formed during the annealing. The growth rates of the $CoSi_2$ nuclei at temperatures ranging from 50 to 150 °C are measured and with which an activation energy of 0.8 ± 0.1 eV is determined. The fact that under our experimental conditions, where nucleation and diffusion are not required and the substrate surface provides additional effective growth sites, the epitaxial $CoSi_2$ can grow on Si(111) at temperatures below 150 °C might lead to useful device applications. Whether this is a general behavior and what the criteria are for the occurrence of this low-temperature growth requires further studies.

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Excimer laser photolysis study of NH_3 and SO_2 mixtures at 193 nm

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Photolysis in the NH_3-SO_2 system was studied by using an ArF excimer laser. The concentration of SO_2 decreases during an irradiation of a mixture of NH_3 and SO_2. It was found from a quadrupole-mass spectroscopic analysis of the photolyzed gases and x-ray diffraction analysis of the solid products that the conversion of SO_2 and NH_3 yields S (solid) and $(NH_4)_2SO_4$.

The photochemistry of sulfur dioxide is of special interest to atmospheric scientists.[1,2] Previous photochemical studies of the mixture of SO_2 and the other molecules have shown that the first excited singlet ($^1B_1$) and the first excited triplet ($^3B_1$) of SO_2 play important roles of SO_2 in the troposphere transformation.[3–9] However, since photochemical reactions induced by using an ordinary light source with a wide range of wavelengths occur via many excitation levels

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